



U.S. DEPARTMENT OF  
**ENERGY**

**Nuclear Energy**

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## **Nuclear Energy University Programs (NEUP) Fiscal Year 2015 Planning Webinar**

**Uranium Resources – Seawater Uranium Recovery**

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# Seawater Uranium Recovery Rationale & Background

- For nuclear energy to remain a sustainable energy source, there must be assurance that an economically viable supply of nuclear fuel is available.
- Seawater contains more than 4 billion tonnes of dissolved uranium.
- This unconventional uranium resource, combined with a suitable extraction cost, can potentially provide a price cap and ensure centuries of uranium supply even with aggressive world-wide growth in nuclear energy applications.

**The challenge is low concentration of uranium in seawater: 3.3 ppb.**

- In the late 1990's, Japanese researches developed braid adsorbent for mooring collection systems.
- Most (~69%) technology costs came from adsorbents materials.



# Braid Adsorbent Deployment

- Dr. M. Tamada of JAEA

## Preparation scheme of graft adsorbent

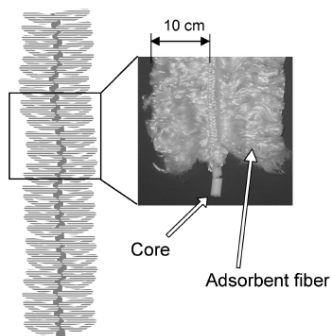
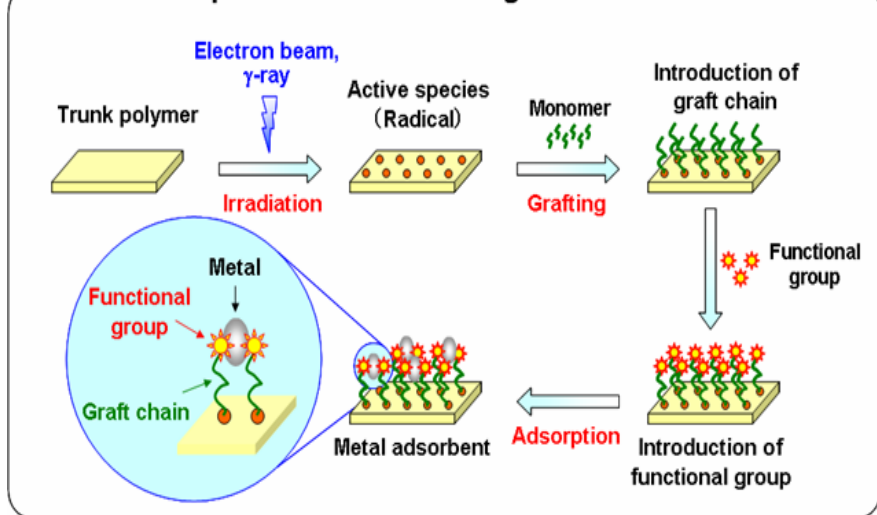
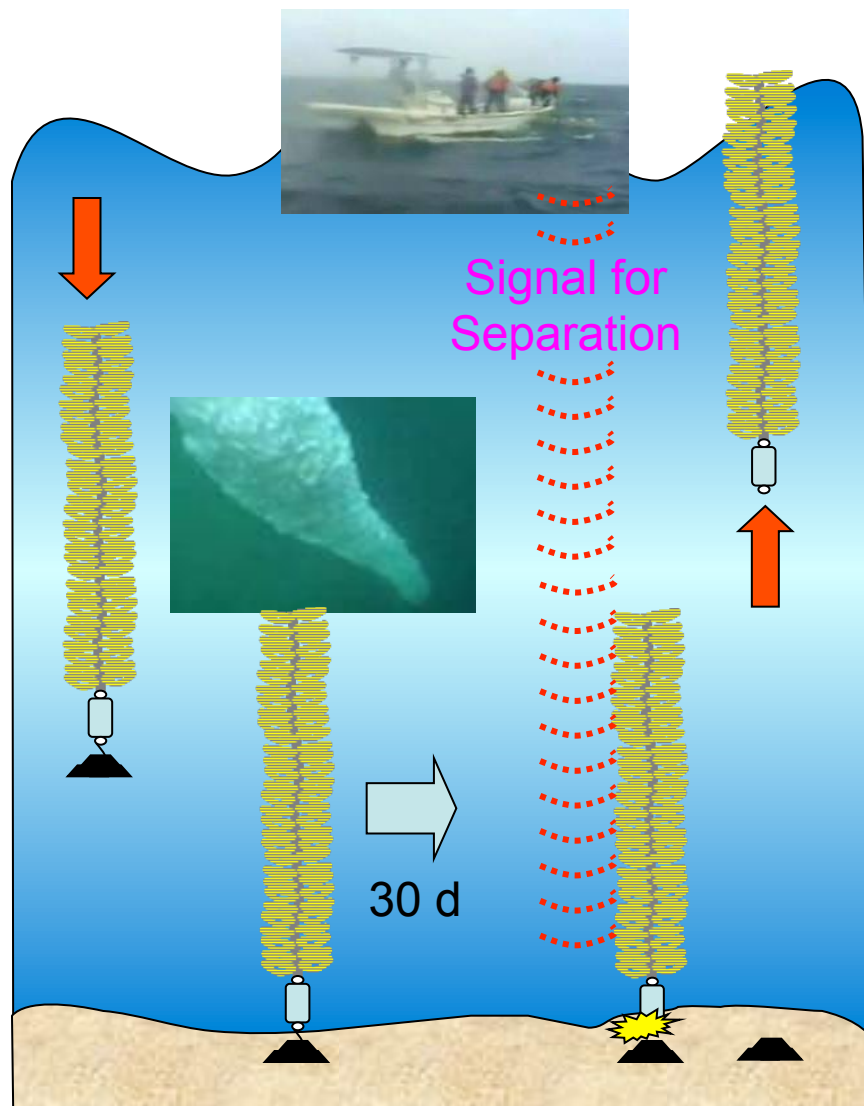
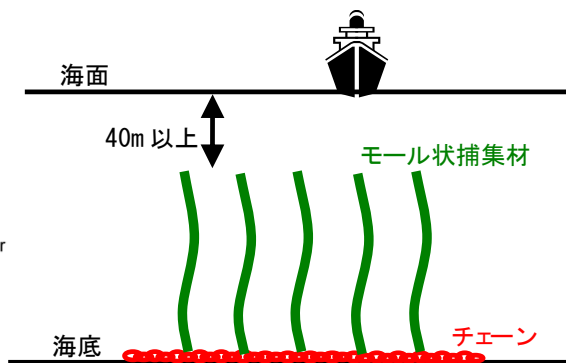


Fig. 1 Braid type adsorbent



# DOE-NE Seawater U Recovery Program

**The DOE-NE started seawater uranium recovery R&D activity in 2011.**

**The research team seeks to take advantage of recent developments in (1) high performance computing, (2) advanced characterization instruments, and (3) nanoscience and nanomanufacturing technology to enable technical breakthroughs. The technology driven, sciences based R&D efforts are focused on:**

- **Synthesizing novel nanoscale adsorbent materials with architectures tailored for specific chemical performance;**
- **Applying quantum beam technologies to understand dynamic chemical processes at the atomic and molecular levels;**
- **Simulating and predicting structural and functional relationships using modern computational tools.**

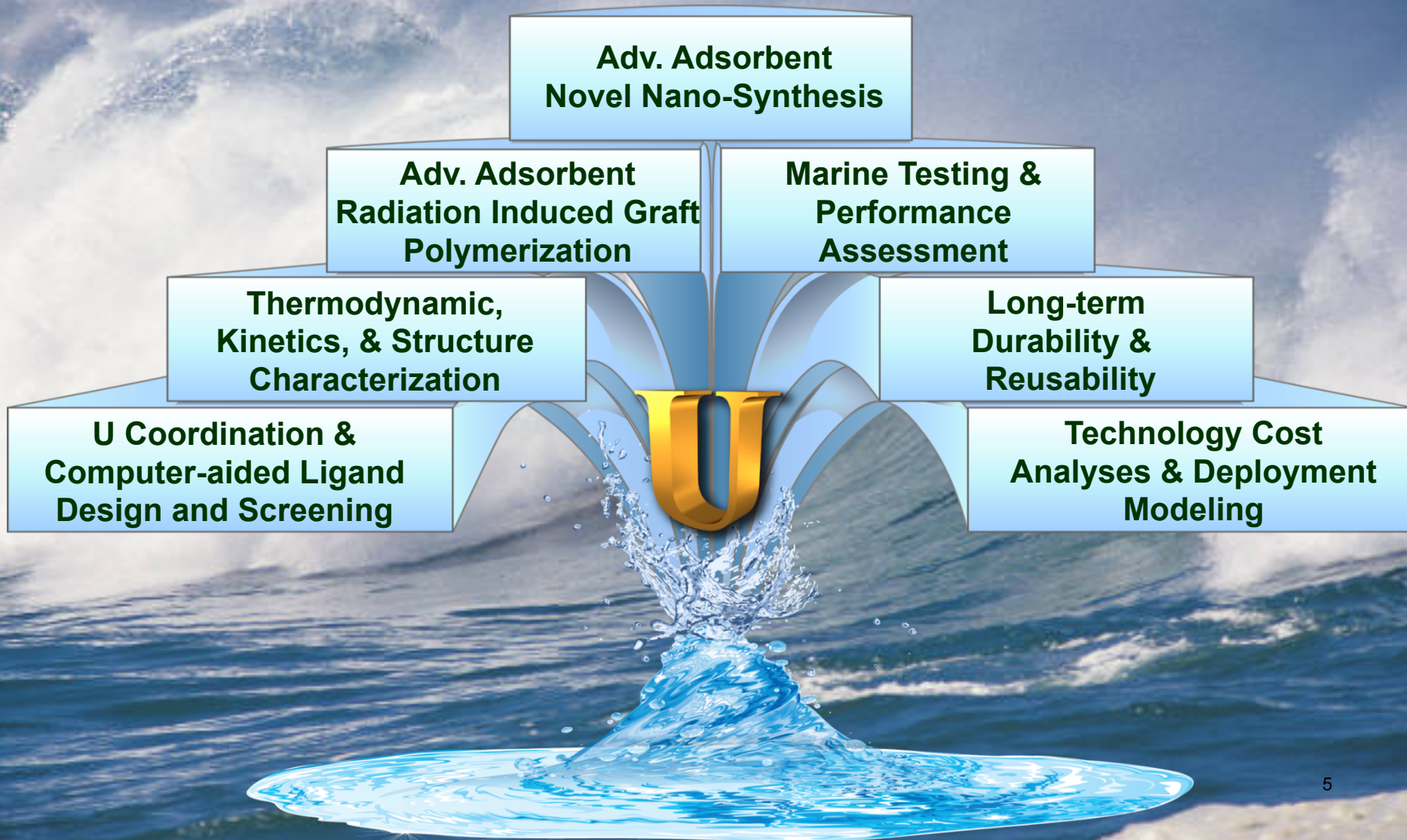
**Program Goals: To develop advanced adsorbents that can simultaneously enhance U sorption capacity, selectivity, kinetics, and materials durability to reduce the technology cost and uncertainties**



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# Seawater U Recovery Program Research Need

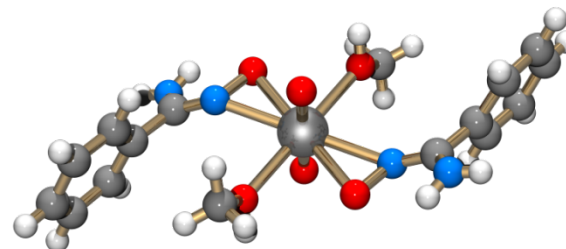
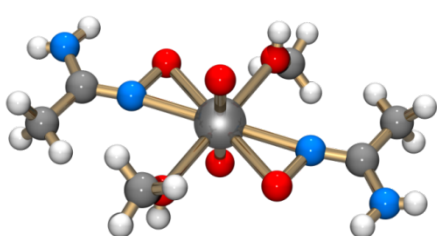




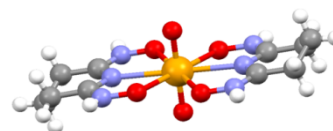
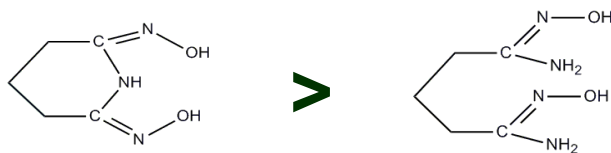
# Research Needs - Understand Binding Structures and Mechanisms

- Uranium exists in seawater as the uranyl ion ( $\text{UO}_2^{2+}$ ) bound to carbonate  $\text{UO}_2(\text{CO}_3)_3^{4-}$
- The uranyl ion binds to two adjacent amidoxime ligands on the adsorbent material to form a chelate complex

**X-ray diffractions of amidoximate-uranyl complexes show  $\eta^2$  binding**



**Closed (cyclic imidedioxime) vs Open (bis-amidoxime) Amidoxime Ligands**



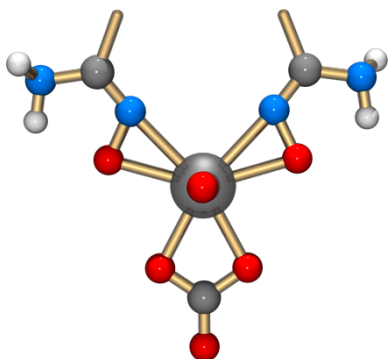
“How Amidoximate Binds the Uranyl Cation”, Vukovic, S.; Watson, L. A.; Kang, S. O.; Custelcean, R.; Hay, B. P. Inorg. Chem. **2012**, 51, 3855-3859.  
Dalton Trans., 2012, 41 (38), 11579. G. Tian, S. J. Teat, Z. Zhang, L. Rao, Sequestering Uranium from Seawater: Binding Strength and Modes of Uranyl Complexes with Glutarimidedioxime



# Research Needs – Computer-aided Ligand Design and Screening

## INPUT

Molecular fragments  
defining geometry of  
binding interaction(s)

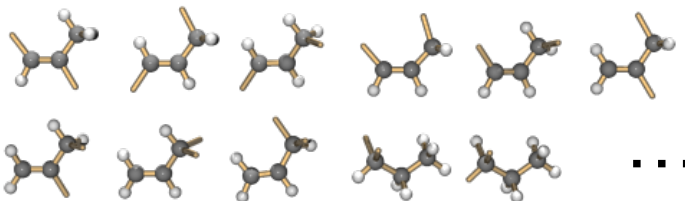


## Computing Tools

*Structure  
generating  
module*

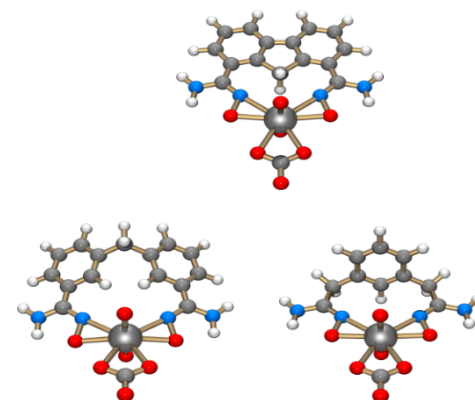
*Scoring  
module*

*Fragment  
library*



## OUTPUT

List of optimal  
structures

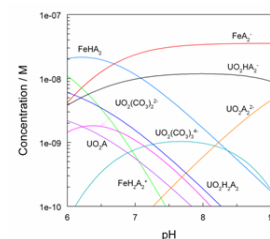
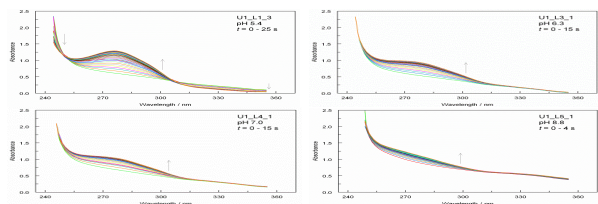


Vukovic, S.; Hay, B. P. "De Novo Structure-based Design of Bis-amidoxime Uranophiles" *Inorg. Chem.* 2013, 52, 7805-7801



# Research Needs – Kinetics and Thermodynamics

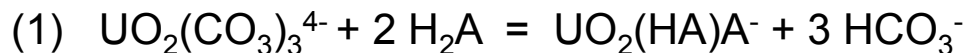
## Kinetics of U(VI) interactions with Amidoxime related ligands



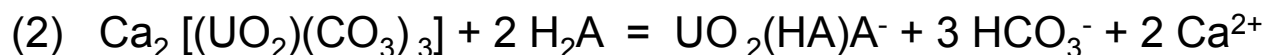
## Competition of U(VI) binding site



## Thermodynamic & Enthalpy Measurements



$$\Delta H = +16.7 \text{ kJ/M}$$



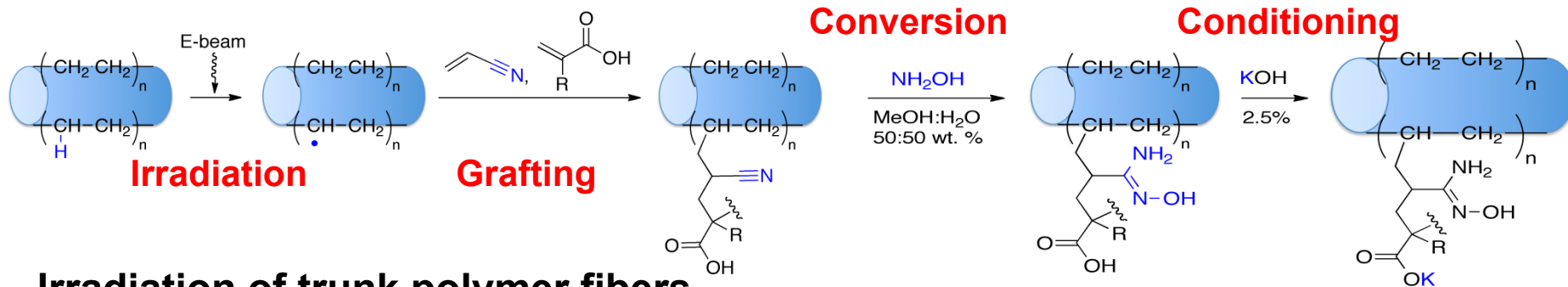
$$\Delta H = +30 \text{ kJ/M}$$

Enthalpy studies suggest an “overall” endothermic reaction under seawater conditions

- Dalton Trans., 2013, 42, 14621-14627. X. Sun, C. Xu, G. Tian, L. Rao, Complexation of glutarimidedioxime with Fe(III), Cu(II), Pb(II), and Ni(II), the competing ions for the sequestration of U(VI) from seawater
- Dalton Trans., 2014, 43 (2), 551. X. Sun, G. Tian, C. Xu, L. Rao, S. Vukovic, S. O. Kang, B. P. Hay, Quantifying the binding strength of U(VI) with phthalimidedioxime in comparison with glutarimidedioxime: Implications in the extraction of U(VI) from seawater with amidoxime-based sorbents
- Chem. Eur. J., 2014, in press. F. Endrizzi, L. Rao, Formation of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  Complexes with  $(\text{UO}_2)(\text{CO}_3)_3^{4-}$  in Aqueous Solution: Effect on the Speciation of U(VI) and its Extraction from Marine Environments.



# Research Needs – Radiation-induced Grafting Polymerization Technology



## Irradiation of trunk polymer fibers

Forms reactive free radicals on polyethylene fiber (energy sources, dosage, rate)

## Grafting of monomers

Polymerization of acrylonitrile and hydrophilic methyl acrylic acid (solvent/additives; co-monomers/ratio)

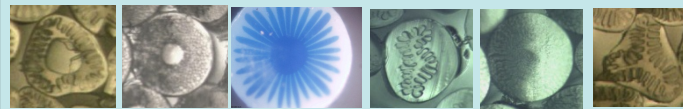
## Functional group conversion - amidoxime

Hydroxylamine to form amidoxime and imidedioxime groups

## Conditioning

Swells adsorbent, forms micropores and converts adjacent AO groups to imidedioxime

## Impact on altering polyethylene fiber diameter and morphology



**Non-round shaped fibers (0.24 - 30  $\mu\text{m}$  dia.) have 2 - 60X higher surface area than 20  $\mu\text{m}$  dia. round fibers**



## Research Needs – Technology Cost Analyses

Parallel to the R&D efforts, U recovery cost analyses, in \$/kg U, are conducted to assess the technology potentials

The objective of cost analyses study:

- Identify highest-impact components of the system
- Guide / prioritize R&D efforts to reduce the technology cost
- Establish technology price threshold

**2006 JAEA analysis<sup>+</sup>: 88,000 yen/kg U (ca. \$1,000/kg U)**

**2011 US analysis<sup>++</sup>: \$1,230/kg U**

**2013 US analysis<sup>+++</sup>: \$610 /kg U**

+ M. Tamada et al., 2006. *Cost Estimation of Uranium Recovery from Seawater with System of Braid Type Adsorbent*. Trans. Atomic Energy Society of Japan, 358-363.

++ E. Schneider, D. Sachde, 2013. The Cost of Recovering Uranium from Seawater by a Braided Polymer Adsorbent, *Science and Global Security*, 21, 2.

+++ Schneider, E. A., and H. D. Lindner, "Energy Balance of Uranium Recovery from Seawater," Proceedings of GLOBAL 2013: Nuclear Energy at a Crossroads, 9 pp., Salt Lake City, UT, October (2013).

Schneider, E.A. and H. D. Lindner, 2014. Unconventional Uranium Resources and Production Costs, *Transactions of the American Nuclear Society*, 110, Reno, NV, June 2014.

# Research Needs – Marine Testing

## Adsorbent Performance Assessment

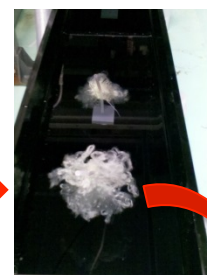
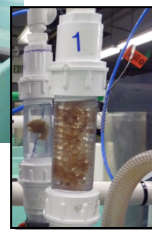
Continuous flow through with fixed bed and flume-type devices to measure the sorption capacity and kinetics

### *Natural Seawater*

- *Salinity*
- *Temperature*
- *Flow-rate/linear velocity*
- *Unfiltered & Filtered*
- *TOC/DOC*
- *Trace Elements*



***Marine Sciences Laboratory,  
Sequim, Washington***



28  
days



To Validate Performance under  
Different Seawater Environments

- ***Woods Hole Oceanographic Institution, Massachusetts***
- ***Broad Key Island, University of Miami, Florida***



- **DOE NE has assembled a multidisciplinary team in 2011 to better understand the potential of the seawater uranium recovery technology.**
- **U.S. investment strategies include:**
  - Developing novel adsorbent materials using high performance computing, advanced characterization instruments, and nanoscience and nanomanufacturing technology;
  - Achieving a molecular-level understanding of ligand coordination modes, sorption mechanisms, kinetics, and thermodynamics.
- **Economic analyses have been used to guide the technology development and to highlight what parameters have the largest impact on the technology cost.**
- **Continue improving sorption capacity, selectivity, kinetics, and materials durability is expected to further reduce the technology cost.**